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(54) **Dispersant.**(30) Priority: **04.09.87 NL 8702089**(43) Date of publication of application: **12.04.89 Bulletin 89/15**(45) Publication of the grant of the patent: **10.11.93 Bulletin 93/45**(84) Designated Contracting States: **AT BE CH DE ES FR GB IT LI NL SE**

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Description

The present invention relates to a solution of a polymer, or organic salts thereof, suitable as dispersants, which polymers contain heterocyclic groups having at least one basic ring nitrogen.

The invention also relates to the use of such polymer solutions for the production of coatings and printing inks, pigment dispersions as well as powdered solids coated with the dispersant according to the invention.

The introduction of solids into liquid media requires high mechanical forces. This depends substantially on the wettability of the solid by the surrounding medium and on the affinity to this medium. For the purposes of reducing these dispersing forces it is conventional to use dispersants facilitating the dispersion. These are mostly surfactants or tensides having an anionic, cationic or a non ionic structure. These agents are directly applied to the solid or added to the dispersing medium in relatively small amounts.

It is further known that these solids tend to flocculate following the dispersion, which nullifies the work earlier done and leads to serious problems. These problems have been accounted for by the London/van der Waal's forces by which the solids attract each other. For the purposes of counteracting these attractive forces absorption layers must be applied to the solid. This is done by using such tensides.

During and following the dispersion there is an interaction between the surrounding medium and the solid particle, resulting in a desorption of the tenside by exchange for the surrounding medium present in a higher concentration. This medium, however, is not capable in most cases of building up such stable absorption layers, resulting in a crash of the whole system. This becomes apparent by the increase in viscosity in liquid systems, losses of gloss and color shifts in lacquers and coatings as well as insufficient color force development in pigmented synthetics.

To solve this problem, e.g., EP-A 154,678, EP-A 74080, US-A 4,032,698 and DE-A 24 38 414 propose dispersants. These dispersants, however, only lead to a partial solution, particularly with respect to the miscibility without flocculation of different pigments with each other, such as organic pigments and inorganic pigments. Moreover, the pigment pastes prepared by the methods defined tend to interact with the surrounding medium, e.g., after use in lacquers. Consequently, it can be assumed that the absorption layers built up only have insufficient stability against desorption. A number of dispersants proposed in these publications further have the drawback that the storage stability is too poor, which leads to precipitation, phase separation, crystallization, etc. This results in that such products are inhomogeneous and useless in practice after a relatively short time.

GB-A 883.750 is directed to a stable aqueous copolymer emulsion comprising a specific quaternary vinyl pyridinium monomer copolymerized in water with styrene, methylacrylate or other monomers, said copolymer containing from 0.2 to 5% of quaternary nitrogen.

US-A 2,721,852 relates to quaternary interpolymers containing vinyl pyridine or vinylquinoline.

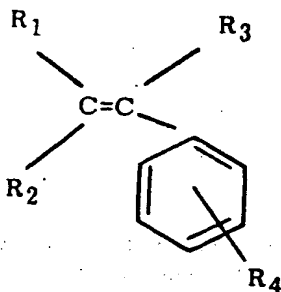
The object of the present invention is to find dispersants which do not show the above described drawbacks or in which these drawbacks have been considerably reduced.

The second object is to find a dispersant having excellent compatibility with a wide range of different binders, especially binders on a polyacrylate basis and air drying alkyd resins.

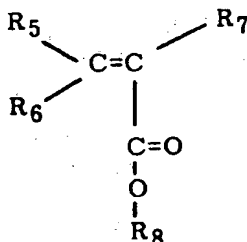
It is also an object of the invention to find a dispersant capable of being used in the production of binder-free pigment dispersions without further binder additives during the dispersing process.

These objects are attained according to the invention by a polymer solution in organic solvent suitable as dispersant, said polymer comprising

A) 5-80 mol% of one or more monomers having the formula



in which R_1 , R_2 , R_3 and R_4 may be the same or different and represent H or alkyl,
B) up to 70 mol% of one or more monomers having the formula



in which R_5 , R_6 and R_7 may be the same or different and represent H or alkyl and R_8 is alkyl or substituted alkyl, and the alkyl chain may also be interrupted by - O - groups,

C) 5-50 mol % of one or more monomers containing a heterocyclic group having at least one basic ring nitrogen atom or to which such a heterocyclic group is attached following polymerization,

D) 0-10 mol % of one or more monomers containing one or more groups reactive to crosslinking or coupling, and

E) 0-20 mol % of one or more monomers not falling within the groups A-D, the amount of monomers from group A together with monomers containing an acrylate group being at least 20 mol%, and A and B are both present as well as organic salts thereof.

The solutions of the polymers have excellent compatibility with all kinds of binders for coatings and printing inks, more in particular with binders on a polyacrylate basis and on an alkyd basis.

Pigment dispersions stabilized with the polymers are distinguished by a high resistance to flocculation, good rheological properties as well as a proper strength of color and a high gloss.

The solution according to the invention can be added in relatively small amounts, to the material to be ground for the dispersing process. The optimum activity of the polymer compound according to the invention is obtained at concentrations of preferably 1 mg to 10 mg, based on 1 m² BET surface of the pigment.

The solution according to the invention can also be used without further binder additives during the dispersing process.

The polymer present in the solution then adopts the function of a dispersing resin. Thus binder-free pigment dispersions are obtained which, in the further applications thereof in coatings and printing inks, have excellent compatibility and do not entrain unnecessary, disturbing dispersing resins.

Optimum results are obtained at a polymer solution/pigment weight ratio of 1 : 1.5 to 1 : 3 with organic pigments and 1 : 4 to 1 : 8 with inorganic pigments.

The products according to the invention consist of a polymer chain having attached thereto the heterocyclic groups with basic nitrogen atoms. Such a chain can be obtained either by polymerizing-in compounds containing both a vinyl and such a heterocyclic group, or by later attaching a heterocyclic group to the polymer chain containing corresponding reactive groups.

Preferred are compounds with basic nitrogen groups having a pKa value of 2 to 14, more in particular 5 to 14 and most preferably 5 to 12. These pKa values relate to the measurement thereof at 25°C in a 0.01 molar concentration in water. These basic groups impart to the dispersants according to the invention a basicity as is also known in this technical field. These basic groups allow the dispersants to form organic salts too. The dispersants can therefore be used in the form of such salts.

These salts are obtained by neutralization of the polymer with organic acids, e.g., aromatic acids having not more than 25 C atoms or aliphatic and cycloaliphatic acids having not more than 22 C atoms. Preference is given to salts of the polymer with organic monocarboxylic acids.

Suitable compounds to be polymerized-in are, e.g., vinylimidazole, vinylpyridine, 2-methyl-N-vinylimidazole, vinylpyrrolidone and vinylcarbazole.

Suitable compounds containing at least one basic nitrogen atom and capable of being attached to a polymer chain are described in, among others, EP-A 154,678.

Examples are inter alia: 1-(2-hydroxyethyl)-pyrrolidine, 2-(1-pyrrolidyl)-ethylamine, 2-(1-piperidyl)-ethylamine, 1-(2-hydroxyethyl)-piperidine, 1-(2-aminopropyl)-piperidine, N-(2-hydroxyethyl)-hexamethylenimin, 4-(2-hydroxyethyl)-morpholine, 2-(4-morpholinyl)-ethylamine, 4-(3-aminopropyl)-morpholine,

1-(2-hydroxyethyl)-piperazine, 1-(2-aminoethyl)-piperazine, 1-(2-hydroxyethyl)-2-alkylimidazoline, 1-(3-aminopropyl)-imidazole, (2-aminoethyl)-pyridine, (2-hydroxyethyl)-pyridine, (3-hydroxypropyl)-pyridine, (hydroxymethyl)-pyridine, N-methyl-2-hydroxymethyl-piperidine, 1-(2-hydroxyethyl)-imidazole, 2-amino-6-methoxybenzothiazole, 4-aminomethyl-pyridine, 4-amino-2-methoxypyrimidine, 2-mercaptopyrimidine, 2-mercapto-benzimidazole, 3-amino-1,2,4-triazole, 2-isopropyl-imidazole, 2-ethyl-imidazole, 4-methyl-imidazole, 2-methyl-imidazole, 2-ethyl-4-methyl-imidazole, 2-phenyl-imidazole and 4-nitro-imidazole.

For use in the polymers it is necessary that these compounds contain at least one reactive group. This may be, for instance, -OH, -NH₂, -NHR, -COOH and -SH. In general, a hydrogen atom reactive to epoxy or isocyanate is required. By means of a reaction with diisocyanate, diepoxyd, diol, dicarboxylic acid, hydroxycarboxylic acid, aminocarboxylic acid, amino-ol, etc. the heterocyclic compound can be coupled to the polymer chain. Tri- or higher functional compounds can also be used, but this does not give important advantages. It is of course also possible to operate without a coupling compound and to directly attach the heterocyclic groups-containing compound to the chain. The compounds polymerizable-in that are suited for this purpose are, e.g., 2-hydroxyethylacrylate, 2-hydroxypropylacrylate, glycidylmethacrylate, 2-hydroxyethylmethacrylate, 2-hydroxypropylmethacrylate, acrylic acid, methacrylic acid, alkoxyated -OH-functional reaction products thereof, etc.

The content of heterocyclic groups-containing monomers, or monomers to which the heterocyclic groups can be attached, ranges between 5 and 50 mol %, preferably between 25 and 40 mol %.

Preferred is the use of vinylimidazole, because in the first place it is easiest with this compound to prepare the polymers and in the second place the dispersants prepared therewith have excellent properties.

The other components of the polymer chain aim at providing optimum compatibility with binders and/or solvents as conventional for coatings and printing inks.

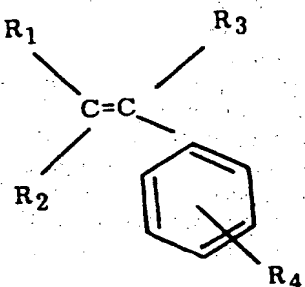
The polymer chain can advantageously comprise at least one monomer of the acrylate type. Suitable monomers are the esters of acrylic acid and methacrylic acid as well as reaction products of ethylene oxide and/or propylene oxide therewith. In this respect it is observed that such reaction products may be both OH- and alkyl-terminated. It is intended in this connection that these reaction products be either alkyl-terminated or, if they are OH-terminated, so little reactive that they do not give rise to further reactions. If these alkoxyated products are reactive, they should be comprised by groups C or D.

Monomers that can be suitably used are, e.g., methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, hexyl methacrylate, 2-ethyl hexyl methacrylate, dimethyl aminoethyl methacrylate, cyclohexyl methacrylate, methylacrylate, isobornyl methacrylate, ethyl acrylate, butyl acrylate, 2-ethyl hexyl acrylate, cetyl methacrylate, stearyl methacrylate, behenyl methacrylate, polypropylene glycol monomethacrylate, polyethylene glycol monomethacrylate and EO-PO-monomethacrylate.

The selection of the monomers is determined by the compatibility of the polymer chain with binder/solvent. One of the monomers preferred is methyl methacrylate, since this monomer provides good compatibility and good film properties. Monomer mixtures can also be used.

The amount of monomer of the acrylate type ranges between 0 and 70 mol %, the amount being determined by inter alia the molecular weight of the monomers. In case of a higher molecular weight, e.g., monomers with an EO-PO chain, a smaller amount is used on a molar base.

A group of monomers that is present concerns the vinylaromatic monomers, such as styrene, α -methyl styrene, vinyl toluene, etc. In general, this group can be defined by the formula



in which R₁, R₂ and R₃ may be H or (C₁-C₄) alkyl. The nucleus substitution R₄ may be absent (R₄ = H) or consist of methyl or higher alkyl (such as C₂-C₁₈).

This group of monomers affects the compatibility with the binders and solvents. Monomers from this group can be used in amounts of 5 to 80 mol%. Preferred are amounts up to 25 mol%, more in particular 5-15 mol%.

According to the present invention the monomers from this group of vinylaromatic compounds and the monomers of the acrylate type are both present. The amount of monomers from group A together with monomers containing acrylate groups are at least 20 mol%.

A next group of monomers is the group used for intercoupling two or more substantially linear polymer chains. In specific cases it may be advantageous, e.g., from the viewpoint of preparation, to prepare relatively low molecular polymers and to interconnect them by means of reactive monomers. For this purpose, in principle the same monomers can be used as described above for attaching heterocyclic groups to the polymer chain.

In general, these monomers are used only in those cases in which a crosslinking or coupling is to be obtained. It is of course possible to combine the monomer groups C and D and to use excess monomer relative to the heterocyclic groups. Thus it is preferably possible first to attach the heterocyclic groups and then to carry out the coupling process.

The amount of monomers from group D depends on the desired molecular weight. In general, not more than about 2-4 reactive groups are required per polymer chain. The coupling can be effected by reaction of the polymerized-in monomers with each other or by using a di- or trifunctional compound as described in relation to the attachment of the heterocyclic group to the chain.

The last group of monomers present only in relatively small amounts, i.e. 0-20 mol %, preferably 0-10 mol %, more in particular 0-5 mol %, preferably 0 mol %, comprises the monomers that are not comprised by groups A-D, such as acrylamide, methacrylamide, vinyl ester, vinyl ether, acrylonitrile, etc. These monomers can be used for finely adjusting the dispersant properties.

The polymers can be prepared in the conventional manner, e.g., by mass or solution polymerization. The polymerization in a solvent is preferred in view of the controllability of the polymerization and the viscosity of the final product. Suitable solvents are DMSO, THF, DMF, ethyl, propyl, butyl, acetate, benzene, toluene, xylene, N-butanol, isobutanol, isopropanol, MEK, MIBK, and acetone.

The monomers are preferably polymerized using a radical reaction, by addition of peroxides, optionally in the presence of redox systems.

The polymerization time depends on the temperature and the desired final product properties but is preferably within the range of from 0.5 to 10 hours at temperatures ranging from 50 to 190°C. The polymerization can be carried out continuously, discontinuously or semicontinuously. If it is preferred to obtain a polymer chain having random distribution of monomers, all of the monomers together will be preferably added to the reaction mixture. This may be done in one portion or in the course of time.

On the basis of the reactivity of the monomers, which is known, a skilled worker can control the polymerization so as to obtain the desired distribution.

The present solution of polymers suitable as dispersants have an excellent dispersing effect. The compatibility with all types of binders for coatings and printing inks is excellent. By suitably selecting monomers a substantially universal dispersant is obtained.

The solutions according to the invention can be used for the production of aqueous and non-aqueous coatings, such as paints and printing inks. They are not water-soluble but may have a self-emulsifying effect in water, so that these are suitable for use in aqueous coatings and printing inks too. In this connection aqueous coatings and printing inks, as used herein, also refer to those products which partially comprise organic cosolvents.

The dispersant is surprisingly superior to known agents built up on the basis of isocyanate, although rather simple raw materials have been used.

With the dispersants pigments that are hard to stabilize can be stabilized without any problems. Also pigment mixtures can be stabilized without causing problems. Following stabilization with the dispersants according to the invention the pigments show a very high resistance to flocculation and impart to a lacquer film containing the pigments an excellent gloss.

Pigments used in this field are the organic and inorganic pigments insoluble in the employed liquid, e.g., soot, polycyclic pigments, iron oxides, etc.

The invention also relates to pigment dispersions, i.e., mixtures of pigment, solution according to the invention and water and/or non-aqueous liquid. These dispersions are sometimes also referred to as binder-free pigment dispersions or pigment slurries. As non-aqueous liquids, use is made of the organic solvents conventional in the field of coatings and printing inks. The amounts of pigment range between 10 and 70 % by weight, and the amounts of solution range between 1 and 10 % by weight.

EXAMPLE 1

In a reaction flask with reflux condenser suitable for polymerization were dissolved in 9.86 g xylene and 4.93 g methoxypropyl acetate 2.84 g vinyl toluene, 4.55 g isobutyl methacrylate, 7.36 g ethyl hexyl acrylate, 5.20 g hydroxyethyl methacrylate, 1.80 g polyethylene glycol monomethacrylate having a molecular weight of approximately 400 and 0.44 g ditertiary butyl peroxide. Polymerization was effected at the boiling point of the mixture while stirring and introducing an inert gas. At the end of the polymerization 9.79 g isophoron diisocyanate were dissolved in 16.58 g isobutyl acetate and 16.58 g methoxypropyl acetate, and the remaining free NCO groups were then converted with 3.60 g polyethylene glycol monomethacrylate having a molecular weight of approximately 400 and 4.51 g 1-(3-aminopropyl)imidazole.

The solid content was then adjusted to 40 % by weight with butylacetate.

EXAMPLE 2

In the manner comparable with Example 1 3.54 g vinyl toluene, 5.69 g isobornyl methacrylate, 9.20 g 2-ethyl hexyl methacrylate, 7.15 g hydroxy ethyl methacrylate, and 1.28 g ditertiary butylperoxide dissolved in 11.94 g xylene and 5.97 g methoxypropyl acetate were polymerized.

Subsequently, 12.23 g isophoron diisocyanate dissolved in 20.36 g butylacetate and 20.36 g methoxypropyl acetate were added. The then remaining free NCO groups were converted with 4.50 g polyethylene glycol monomethacrylate having a molecular weight of approximate 400 and 3.78 g 3-amino-1,2,4-triazole in 11.34 g N-methylpyrrolidone.

The solid content was then adjusted to 40% by weight with butylacetate.

EXAMPLE 3

In the manner described in Example 1 6.66 g isobornyl methacrylate, 5.46 g cyclohexyl methacrylate, 6.40 g butylacrylate, and 7.85 g hydroxy ethyl methacrylate were polymerized with 1.28 g ditertiary butyl peroxide dissolved in 11.98 g xylene and 5.99 g methoxypropyl acetate. To this polymer containing hydroxyl groups 12.23 g isophoron diisocyanate dissolved in 20.4 g butylacetate and 20.40 g methoxypropyl acetate were added. The free NCO groups were then converted with 4.50 g polyethylene glycol monomethacrylate and 5.54 g 2-(2-pyridyl)-ethanol.

The solid content was then adjusted to 40 % by weight with xylene.

EXAMPLE 4

In the manner described in Example 1 a polymerization of 3.78 g vinyl toluene, 5.69 g isobutyl methacrylate, 7.38 g 2-ethyl hexyl methacrylate, 7.97 g stearyl methacrylate, 4.55 g glycidyl methacrylate and 0.59 g ditertiary butylperoxide was effected in 14.98 g xylene and 4.99 g methoxypropyl acetate.

At the end of the polymerization 24.97 g butylacetate were added, and 4.01 g 1-(3-aminopropyl)imidazole were added to the polymer.

EXAMPLE 5

In the manner described in Example 1 a polymerization of 6.66 g isobornyl methacrylate, 5.46 g cyclohexyl methacrylate, 9.96 g stearyl methacrylate, 9.22 g 2-ethyl hexyl methacrylate, 5.69 g glycidyl methacrylate and 0.74 g ditertiary butylperoxide was effected in 18.86 g xylene and 6.29 g methoxypropyl acetate.

At the end of the polymerization 18.94 g butyl acetate were added, and 4.05 g 3-mercapto-1,2,4-triazole dissolved in 16.20 g N-methyl pyrrolidone were added to the polymer.

EXAMPLE 6

In the manner described in Example 1 a polymerization of 12.0 g methyl methacrylate, 32.76 g cyclohexyl methacrylate, 35.84 g butylacrylate, 18.82 g vinyl imidazole and 2.0 g tertiary butyl perbenzoate was effected in 50.71 g xylene and 16.91 g n-butanol.

The solid content was adjusted to 40 % by weight with butyl acetate.

EXAMPLE 8

In 15.67 g secondary butanol and 47.0 g butyl acetate were polymerized in the manner described in Example 1: 29.97 g isobornyl methacrylate, 9.36 g styrene, 38.71 g 2-ethyl hexyl acrylate, 14.12 g vinyl imidazole, 0.62 g tertiary butyl-per-2-ethyl hexoate and 1.23 g tertiary butyl perbenzoate.

At the end of the polymerization the solid content was adjusted to 50 % by weight by means of butyl acetate.

EXAMPLE 9

In 45.08 g xylene and 22.54 g n-butanol, 12.00 g methyl methacrylate, 32.76 g cyclohexyl methacrylate, 35.84 g butyl acrylate, 18.82 g vinyl imidazole and 2.0 g tertiary butyl perbenzoate were polymerized in the manner described in Example 1.

At the end of the polymerization the solid content was adjusted to 50 % by weight by adding 33.80 g xylene.

EXAMPLE 10

In 47.00 g toluene and 15.67 g n-butanol, 29.97 g isobornyl methacrylate, 9.36 g styrene, 38.71 g 2-ethyl hexyl acrylate, 14.12 g vinyl imidazole and 11.85 g tertiary butyl perbenzoate were polymerized in the manner described in Example 1.

At the end of the polymerization a polymer solution was obtained having a solid content of 60% by weight.

EXAMPLE 11

In 43.75 g xylene and 14.59 g n-butanol, 23.31 g isobornyl methacrylate, 31.35 g butyl acrylate, 10.92 g styrene, 3.71 g acrylonitrile, 16.47 g vinyl imidazole and 1.72 g tertiary butyl perbenzoate were polymerized.

At the end of the polymerization the solid content of the polymer solution was adjusted to 50% by weight by adding xylene.

EXAMPLE 12

In the manner described in Example 1, 19.98 g isobornyl methacrylate, 10.62 g vinyl toluene, 30.42 g 2-ethyl hexyl acrylate, 6.75 g polyethylene glycol monomethacrylate, 16.38 g cyclohexyl methacrylate, 15.53 g vinyl imidazole, 0.67 g tertiary butyl peroctoate and 1.34 g tertiary butyl perbenzoate were polymerized in 50.85 g butyl acetate and 16.95 g secondary butanol.

At the end of the polymerization the solid content of the polymer solution was adjusted to 50% by weight with butyl acetate.

EXAMPLE 13

In 98.67 g butyl acetate and 19.74 g n-butanol the following substances were polymerized in the manner described in Example 1: 19.98 g isobornyl methacrylate, 10.92 g cyclohexyl methacrylate, 10.62 g vinyl toluene, 15.0 g methyl methacrylate, 6.75 g polyethylene glycol monomethacrylate, 14.12 g vinyl imidazole and 1.56 g tertiary butyl perbenzoate.

At the end of the polymerization the solid content of the solution was adjusted to 40% by weight by adding butyl acetate.

To evaluate the behaviour of the dispersants according to the invention, these were used in three different lacquer systems, while also comparing with the dispersant according to Example 14 of EP-A-154,678.

The compositions of the three lacquer systems are listed in the following Table 1.

TABLE 1

5	lacquer system A = 2 components acrylate.		
	<u>Component 1</u>		
	MACRYNAL 510 N, 60 % (acrylic resin, Hoechst, TM)	21.98	parts by wt.
10	ethyl glycol acetate	5.54	
	SOLVESSO 100 (aromatic solvent, TM)	8.89	
	butyl acetate 99/100 %	8.00	
	pigment, organic	1.80 - 5.00	
	dispersant, 50 %	1.25 - 2.50	
	(ditto, 25 %	2.50 - 5.00)	
15	MACRYNAL 510 N, 60 %	39.25	
	DBTL 1 %	0.26	
	xylene	4.29	
	butyl acetate, 99/100 %	4.29	
20		100.00	parts by wt.
	<u>Component 2</u>		
	Hardener, DESMODUR N 75 (isocyanate, Bayer)	25.00	
25	butyl acetate, 99/100 %	20.00	
		145.00	
		=====	
	lacquer system B = enamel on a polyester basis		
30	DYNAPOL H 700, 60 % (oil-free polyester TM)	27.50	parts by wt.
	pigment, organic	1.80 - 5.00	
	SOLVESSO 100	8.00	
	n-butanol	4.00	
	dispersant, 50 %	1.08 - 2.50	
	(ditto, 25 %	2.16 - 5.00)	
35	DYNAPOL H 700, 60 %	25.40	
	MAPRENAL 650, 55 % (melamine resin, TM)	25.52	
	SOLVESSO 100	2.08	
		100.00	parts by wt.
		=====	
40	lacquer system C = air-drying lacquer on an alkyd resin basis		
	ALFTALAT AM 649 m, 60 % (air-drying alkyl resin, TM)	22.00	parts by wt.
	test benzine K 30*	16.00	
45	pigment	1.80 - 5.00	
	dispersant, 50 %	1.08 - 2.50	
	(ditto, 25 %, 2.16-5.00)		
	ALFTALAT AM 649 m, 60 %	39.20	
	test benzine K 30	12.10	
	OCTA SOLIGEN KBM fl. 1:1 (siccative TM)	2.20	
50	anti-skinning agent	1.00	
		100.00	parts by wt.

*see table 3

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By using these three lacquer systems as well as four pigments that are known to be hardly dispersible, a number of pigmented lacquers were prepared using a dispersant according to the present invention, while also comparing with a dispersant according to the state of the art. The results are listed in Table 2, in the

last two columns of which the stability of the pigmented lacquer systems is indicated by a scale of 1-6. A visual evaluation of the behaviour of the lacquer when placed on a glass sheet is given in the column "behaviour film". A visual evaluation of the behaviour of the liquid lacquer is given in the column "behaviour lacquer".

TABLE 2

Pigment	Parts by wt. of pigment	Lacquer sy. m	Dispersant (DM)	Parts by wt. DM, 100 %	Behaviour film	Behaviour lacquer
Gas soot FW 200 DEGUSSA	1.80	A	Example 12	0.54	1	1
			comp. ex.	0.54	2	6
		B	example 12	0.54	1	1
			comp. ex.	0.54	4	4
		C	example 12	0.54	1	1
			comp. ex.	0.54	3	4
PALIOGEN-ROT L 3910 HD BASF	5.00	A	example 12	1.00	3	1
			comp. ex.	1.00	4	6
		B	example 12	1.00	3	3
			comp. ex.	1.00	4	4
		C	example 12	1.00	1	1
			comp. ex.	1.00	4	5
QUINDO VIOLET RV 6926 BAYER	5.00	A	example 12	0.63	1	1
			comp. ex.	0.63	3	6
		B	example 12	0.63	1	1
			comp. ex.	0.63	4	6
		C	example 12	0.63	1	1
			comp. ex.	0.63	4	3
IRGAZIN DPP ROT BO CIBA-GEIGY	5.00	A	example 12	1.25	2	1
			comp. ex.	1.25	6	6
		B	example 12	1.25	1	2
			comp. ex.	1.25	6	6
		C	example 12	1.25	1	1
			comp. ex.	1.25	6	5

Note 1: excellent pigment stability
no flocculation

Note 6: no pigment stability
complete flocculation

Comparative example: Example 14
EP-A 154,678

To evaluate the compatibility of the dispersants according to the invention, it was determined to what extent the dispersants could be diluted with a number of types of test benzines ("white spirit"). In the

following Table 3 it is indicated how many parts of the different test benzines can be added to the dispersant according to Example 12, without the occurrence of precipitation or flocculation.

TABLE 3

	Example 12
Test benzine K 21*	7
Test benzine K 30**	5
Test benzine K 60***	3

*boiling range 135-175 °C

**boiling range 145-200 °C

***boiling range 180-211 °C

For the purposes of comparison it may be indicated that the product used in Table 2 for comparative purposes was hardly soluble in these substances, since precipitation already occurred when adding less than 1 part by weight of test benzine to 1 part by weight of the binder.

To determine the compatibility with oil-modified alkyl resins 1 part of dispersant (solid) was added to 10 parts by weight (solid) of two different binders. The compatibility of the dispersant according to the invention with two oil-modified alkyl resins is indicated in Table 4.

TABLE 4

	Example 12	comparative example
ALFTALAT AM 649 m, 60 % Hoechst AG	+	-
ALKYDAL M 48,55 % Bayer AG.	+	-
+ = compatible		
- = incompatible		

To determine the storage stability at room temperature of the binders according to the invention, the binder according to Example 12 and the binder according to Example 14 of European patent application 154,678 were stored at room temperature. After 8 days, 30 days and 150 days the condition of the binders was evaluated.

The binder according to Example 12 was still clear and liquid after 8, 30 and 150 days.

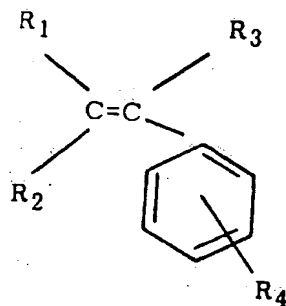
The comparative example showed turbidity after 8 days, turbidity and thickening after 30 days, and turbidity and solidification after 150 days.

It is apparent from the above tests that the dispersants according to the invention show a clearly improved dispersing effect as well as an improved compatibility with oil-modified alkyd resins, improved solubility in aliphatic hydrocarbons and an improved storage stability.

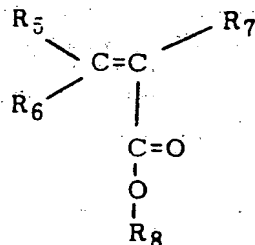
Claims

1. A solution of a polymer in an organic solvent, said polymer comprising

A) 5-80 mol % of one or more monomers having the formula



in which R_1 , R_2 , R_3 and R_4 may be the same or different and represent H or alkyl,
 B) up to 70 mol % of one or more monomers having the formula



in which R_5 , R_6 and R_7 may be the same or different and represent H or alkyl and R_8 is alkyl or substituted alkyl, and the alkyl group R_8 may also be interrupted by - O - groups,

C) 5-50 mol % of one or more monomers containing a heterocyclic group having at least one basic ring nitrogen atom, or to which such a heterocyclic group is attached following polymerization,

D) 0-10 mol % of one or more monomers containing one or more groups reactive to cross-linking or coupling, and

E) 0-20 mol % of one or more monomers not falling within the groups A-D, wherein the amount of A and B together, must be at least 20 mol% and A and B are both present, as well as organic salts thereof.

2. A solution as claimed in claim 1, in which the amount of monomers from group B is at least 20 mol %.

3. A solution as claimed in claim 1 or 2, wherein the polymer consists of:

- 5-15 mol % monomers from group A,
- 25-70 mol % monomers from group B,
- 25-40 mol % monomers from group C,
- 0-5 mol % monomers from group D and
- 0-5 mol % monomers from group E.

4. A solution as claimed in claims 1-3, in which the monomers from group A are selected from vinyl toluene, styrene and α -methyl styrene.

5. A solution as claimed in claims 1-4, in which the monomers from group B are selected from methyl methacrylat, ethyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, hexyl methacrylate, 2-ethyl hexyl methacrylat, dimethyl aminoethyl methacrylate, cyclohexyl methacrylate, methylacrylate, isobornyl methacrylate, ethyl acrylate, butyl acrylate, 2-ethyl hexyl acrylate, cetyl methacrylate, stearyl methacrylat, behenyl methacrylate, polypropylen glycol monomethacrylate, poly thylene glycol

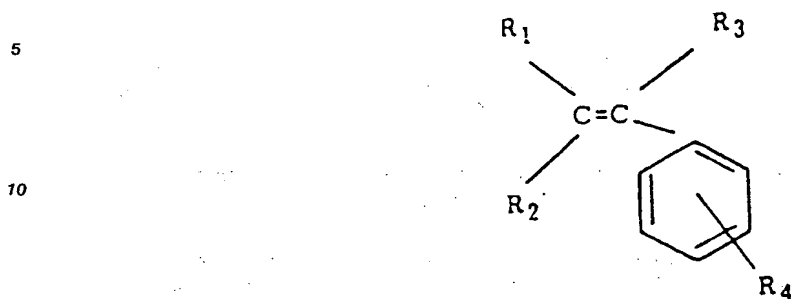
monomethacrylate and EP-PO monomethacrylate.

6. A solution as claimed in claims 1-5, in which the monomers from group C consist of monomers containing a heterocyclic group having at least one basic ring nitrogen atom.
7. A solution as claimed in claim 6, in which said monomers are selected from vinylimidazole, vinylpyridine, 2-methyl-N-vinylimidazole, vinylpyrrolidone and vinylcarbazole.
8. A solution as claimed in claims 1-5, in which the monomers from group C consist of monomers to which following polymerization a compound with a heterocyclic group having at least one basic ring nitrogen atom is attached.
9. A solution as claimed in claim 8, in which the monomers are selected from 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, glycidyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, acrylic acid, methacrylic acid and alkoxylated OH-functional reaction products thereof.
10. A solution as claimed in claim 8 or 9, in which the attached compound is selected from 1-(2-hydroxyethyl)-pyrrolidine, 2-(1-pyrrolidyl)-ethyl amine, 2-(1-piperidyl)-ethylamine, 1-(2-hydroxyethyl)-piperidine, 1-(2-aminopropyl)-piperidine, N-(2-hydroxyethyl)-hexamethylene imine, 4-(2-hydroxyethyl)-morpholine, 2-(4-morpholinyl)-ethylamine, 4-(3-aminopropyl)-morpholine, 1-(2-hydroxyethyl)-piperazine, 1-(2-aminoethyl)-piperazine, 1-(2-hydroxyethyl)-2-alkylimidazoline, 1-(3-aminopropyl)-imidazole, (2-aminoethyl)-pyridine, (2-hydroxyethyl)-pyridine, (3-hydroxypropyl)-pyridine, (hydroxymethyl)-pyridine, N-methyl-2-hydroxymethyl-piperidine, 1-(2-hydroxyethyl)-imidazole, 2-amino-6-methoxybenzothiazole, 4-aminomethyl-pyridine, 4-amino-2-methoxypyrimidine, 2-mercaptopyrimidine, 2-mercapto-benzimidazole, 3-amino-1,2,4-triazole, 2-isopropyl-imidazole, 2-ethyl-imidazole, 4-methyl-imidazole, 2-methyl-imidazole, 2-ethyl-4-methyl-imidazole, 2-phenyl-imidazole and 4-nitro-imidazole.
11. A solution as claimed in claims 1-10, in which the content of monomers from group D is greater than 0 mol % and the monomers are selected from 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, glycidyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, acrylic acid, methacrylic acid and alkoxylated OH-functional reaction products of said compounds.
12. The use of the solution as claimed in claims 1-11 in the production of coatings and printing inks.
13. The use as claimed in claim 12, using 1-10 mg polymer per m² pigment surface (BET).
14. Powdered solids to be incorporated in liquid systems, coated with the polymer as described in claims 1-11.
15. Solids as claimed in claim 14, in which the content of polymer ranges between 1 and 10 mg per m² pigment surface.
16. Pigment dispersions consisting mainly of one or more pigments, a polymer as described in claims 1-11 and water and/or non-aqueous liquid.
17. A pigment dispersion as claimed in claim 16, consisting mainly of 10-70 % by weight of pigment, 1-10 % by weight of said polymer and 20-89% by weight of water and/or non-aqueous liquid.

Patentansprüche

1. Lösung eines Polymeren in einem organischen Lösungsmittel, wobei das Polymere enthält

A) 5 bis 80 Mol-% eines oder mehrerer Monomere mit der Formel



wobei R_1 , R_2 , R_3 und R_4 gleich oder verschieden sein können und H oder Alkyl darstellen,
 B) bis zu 70 Mol-% eines oder mehrerer Monomere mit der Formel



wobei R_5 , R_6 und R_7 gleich oder verschieden sein können und H oder Alkyl darstellen, und es sich bei R_8 um Alkyl oder substituiertes Alkyl handelt, und die Alkylgruppe R_8 auch durch -O-Gruppen unterbrochen sein kann,

C) 5 bis 50 Mol-% eines oder mehrerer Monomere, enthaltend eine heterocyclische Gruppe mit mindestens einem basischen Ring-Stickstoffatom, oder an das bzw. an die eine derartige heterocyclische Gruppe im Anschluß an eine Polymerisation angehängt wird,

D) 0 bis 10 Mol-% eines oder mehrerer Monomere, enthaltend eine oder mehrere zur Vernetzung oder Kopplung reaktive Gruppen, und

E) 0 bis 20 Mol-% eines oder mehrerer Monomere, das bzw. die nicht in die Gruppen A bis D fallen, wobei die Menge an A und B zusammen mindestens 20 Mol-% betragen muß, und A und B beide anwesend sind, sowie organische Salze davon.

2. Lösung nach Anspruch 1, wobei die Menge an Monomeren aus Gruppe B mindestens 20 Mol-% beträgt.

3. Lösung nach Anspruch 1 oder 2, wobei die Polymerlösung besteht aus:

- 5 - 15 Mol-% Monomeren aus Gruppe A,
- 25- 70 Mol-% Monomeren aus Gruppe B,
- 25- 40 Mol-% Monomeren aus Gruppe C,
- 0 - 5 Mol-% Monomeren aus Gruppe D und
- 0 - 5 Mol-% Monomeren aus Gruppe E.

4. Lösung nach einem der Ansprüche 1 bis 3, wobei die Monomeren der Gruppe A aus Vinyltoluol, Styrol und α -Methylstyrol ausgewählt sind.

5. Lösung nach einem der Ansprüche 1 bis 4, wobei die Monomeren der Gruppe B aus Methylmethacrylat, Ethylmethacrylat, n-Butylmethacrylat, Isobutylmethacrylat, Hexylmethacrylat, 2-Ethylhexylmethacry-

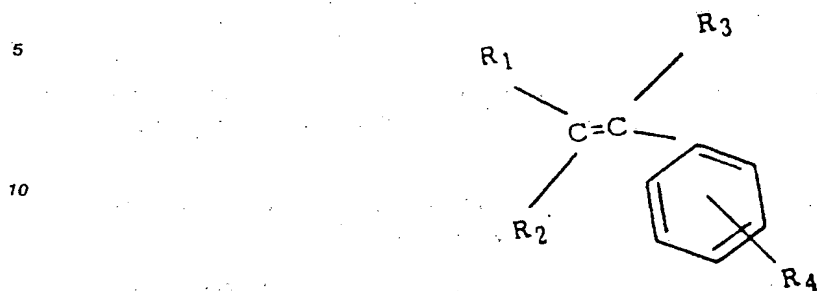
lat, Dimethylaminoethylmethacrylat, Cyclohexylmethacrylat, Methylacrylat, Isobornylmethacrylat, Ethylacrylat, Butylacrylat, 2-Ethylhexylacrylat, Cetylmethacrylat, Stearylacrylat, Behenylmethacrylat, Polypropylenglycolmonomethacrylat, Polyethylenglycolmonomethacrylat und EP-PO-Monomethacrylat ausgewählt sind.

- 5
6. Lösung nach einem der Ansprüche 1 bis 5, wobei die Monomeren der Gruppe C aus Monomeren bestehen, die eine heterocyclische Gruppe mit mindestens einem basischen Ring-Stickstoffatom enthalten.
- 10 7. Lösung nach Anspruch 6, wobei die Monomeren aus Vinylimidazol, Vinylpyridin, 2-Methyl-N-vinylimidazol, Vinylpyrrolidon und Vinylcarbazol ausgewählt sind.
8. Lösung nach einem der Ansprüche 1 bis 5, wobei die Monomeren der Gruppe C aus Monomeren bestehen, an die im Anschluß an eine Polymerisation eine Verbindung mit einer heterocyclischen Gruppe mit mindestens einem basischen Ring-Stickstoffatom angehängt wird.
- 15 9. Lösung nach Anspruch 8, wobei die Monomeren aus 2-Hydroxyethylacrylat, 2-Hydroxypropylacrylat, Glycidylmethacrylat, 2-Hydroxyethylmethacrylat, 2-Hydroxypropylmethacrylat, Acrylsäure, Methacrylsäure und alkoxylierten OH-funktionellen Reaktionsprodukten davon ausgewählt sind.
- 20 10. Lösung nach Anspruch 8 oder 9, wobei die angehängte Verbindung ausgewählt ist aus 1-(2-Hydroxyethyl)-pyrrolidin, 2-(1-Pyrrolidyl)-ethylamin, 2-(1-Piperidyl)-ethylamin, 1-(2-Hydroxyethyl)-piperidin, 1-(2-Aminopropyl)-piperidin, N-(2-Hydroxyethyl)-hexamethylenimin, 4-(2-Hydroxyethyl)-morpholin, 2-(4-Morpholiny)-ethylamin, 4-(3-Aminopropyl)-morpholin, 1-(2-Hydroxyethyl)-piperazin, 1-(2-Aminoethyl)-piperazin, 1-(2-Hydroxyethyl)-2-alkylimidazol, 1-(3-Aminopropyl)-imidazol, (2-Aminoethyl)-pyridin, (2-Hydroxyethyl)-pyridin, (3-Hydroxypropyl)-pyridin, (Hydroxymethyl)-pyridin, N-Methyl-2-hydroxymethyl-piperidin, 1-(2-Hydroxyethyl)-imidazol, 2-Amino-6-methoxybenzothiazol, 4-Aminomethylpyridin, 4-Amino-2-methoxypyrimidin, 2-Mercaptopyrimidin, 2-Mercapto-benzimidazol, 3-Amino-1,2,4-triazol, 2-Isopropylimidazol, 2-Ethylimidazol, 4-Methylimidazol, 2-Methylimidazol, 2-Ethyl-4-methylimidazol, 2-Phenylimidazol und 4-Nitroimidazol.
- 30 11. Lösung nach einem der Ansprüche 1 bis 10, wobei der Gehalt an Monomeren aus Gruppe D größer als 0 Mol-% ist, und die Monomeren aus 2-Hydroxyethylacrylat, 2-Hydroxypropylacrylat, Glycidylmethacrylat, 2-Hydroxymethylmethacrylat, 2-Hydroxypropylmethacrylat, Acrylsäure, Methacrylsäure und alkoxylierten OH-funktionellen Reaktionsprodukten dieser Verbindungen ausgewählt sind.
- 35 12. Verwendung der Lösung nach einem der Ansprüche 1 bis 11 bei der Herstellung von Überzügen und Druckfarben.
- 40 13. Verwendung nach Anspruch 12, wobei 1-10 mg Polymer pro m² Pigmentoberfläche (BET) verwendet werden.
14. Pulverförmige Feststoffe zur Einverleibung in Flüssigsysteme, die mit dem Polymeren, wie in den Ansprüchen 1 bis 11 beschrieben, beschichtet sind.
- 45 15. Feststoffe nach Anspruch 14, wobei der Gehalt an Polymerem im Bereich zwischen 1 und 10 mg pro m² Pigmentoberfläche liegt.
16. Pigmentdispersionen, vorwiegend bestehend aus einem oder mehreren Pigmenten, einem Polymeren wie in den Ansprüchen 1 bis 11 beschrieben und Wasser und/oder einer nichtwäßrigen Flüssigkeit.
- 50 17. Pigmentdispersion nach Anspruch 16, vorwiegend bestehend aus 10 bis 70 Gewichts-% Pigment, 1 bis 10 Gewichts-% des Polymeren und 20 bis 89 Gewichts-% Wasser und/oder nichtwäßriger Flüssigkeit.

55 Revendications

1. Une solution de polymère dans un solvant organique, ledit polymère comprenant

A) 5-80 mol% d'un ou plusieurs monomères de formule



dans laquelle R_1 , R_2 , R_3 et R_4 peuvent être les mêmes ou différents et représentent H ou un groupement alkyle,

B) jusqu'à 70 mol% d'un ou plusieurs monomères de formule



dans laquelle R_5 , R_6 et R_7 peuvent être les mêmes ou différents et représentent H ou un groupement alkyle et R_8 est un groupement alkyle ou alkyle substitué, et le groupement alkyle R_8 peut aussi être interrompu par des groupements -O-

C) 5-50 mol% d'un ou plusieurs monomères contenant un groupement hétérocyclique ayant au moins un atome d'azote cyclique basique, ou auxquels un tel groupement hétérocyclique est attaché après la polymérisation,

D) 0-10 mol% d'un ou plusieurs monomères contenant un ou plusieurs groupements réactifs à la réticulation ou au couplage, et

E) 0-20 mol% d'un ou plusieurs monomères ne tombant dans aucun des groupes A-D, dans laquelle la quantité de monomères de A et B pris ensemble, doit être d'au moins 20 mol%, et A et B sont tous deux présents ainsi que leurs sels organiques.

2. Une solution selon la revendication 1, dans laquelle la quantité de monomères du groupe B est d'au moins 20 mol%.

3. Une solution selon la revendication 1 ou 2, dans laquelle le polymère consiste en :

5-15 mol% de monomères du groupe A,
25-70 mol% de monomères du groupe B,
25-40 mol% de monomères du groupe C,
0-5 mol% de monomères du groupe D et
0-5 mol% de monomères du groupe E.

4. Une solution selon les revendications 1-3, dans laquelle les monomères du groupe A sont choisis parmi le vinyltoluène, le styrène et l' α -méthylstyrène.

5. Une solution selon les revendications 1-4, dans laquelle les monomères du groupe B sont choisis parmi les méthacrylate de méthyle, méthacrylate d'éthyle, méthacrylate de n-butyle, méthacrylate d'isobutyle,

méthacrylate d'hexyle, méthacrylate de 2-éthylhexyle, méthacrylate de diméthylaminoéthyle, méthacrylate de cyclohexyle, méthylacrylate, méthacrylate d'isobornyle, acrylate d'éthyle, acrylate de butyle, acrylate de 2-éthylhexyle, méthacrylate de cétyle, méthacrylate de stéaryle, méthacrylate de béhényle, monométhacrylate de polypropylène glycol, monométhacrylate de polyéthylène glycol et monométhacrylate EO-PO.

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6. Une solution selon les revendications 1-5, dans laquelle les monomères du groupe C consistent en des monomères contenant un groupement hétérocyclique ayant au moins un atome d'azote cyclique basique.

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7. Une solution selon la revendication 6, dans lequel lesdits sont sélectionnés parmi le vinylimidazole, la vinylpyridine, le 2-méthyl-N-vinylimidazole, la vinylpyrrolidone et le vinylcarbazole.

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8. Une solution selon les revendications 1-5, dans laquelle les monomères du groupe C consistent en des monomères auxquels après la polymérisation on attache un composé avec un groupement hétérocyclique ayant au moins un atome d'azote cyclique basique.

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9. Une solution selon la revendication 8, dans laquelle les monomères sont choisis parmi l'acrylate de 2-hydroxyéthyle, l'acrylate de 2-hydroxypropyle, le méthacrylate de glycidyle, le méthacrylate de 2-hydroxyéthyle, le méthacrylate de 2-hydroxypropyle, l'acide acrylique, l'acide méthacrylique et leurs produits réactionnels alkoxylés à fonction -OH.

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10. Une solution selon les revendications 8 ou 9, dans laquelle le composé qu'on attache est choisi parmi les composés suivants : 1-(2-hydroxyéthyl)-pyrrolidine, 2-(1-pyrrolidyl)-éthylamine, 2-(1-pipéridyl)-éthylamine, 1-(2-hydroxyéthyl)-pipéridine, 1-(2-aminopropyl)-pipéridine, N-(2-hydroxy-éthyl)-hexaméthylènimine, 4-(2-hydroxyéthyl)-morpholine, 2-(4-morpholiny)-éthylamine, 4-(3-aminopropyl)-morpholine, 1-(2-hydroxyéthyl)-pipérazine, 1-(2-aminoéthyl)-pipérazine, 1-(2-hydroxyéthyl)-2-alkylimidazoline, 1-(3-aminopropyl)-imidazole, (2-aminoéthyl)-pyridine, (2-hydroxyéthyl)-pyridine, (3-hydroxypropyl)-pyridine, (hydroxyméthyl)-pyridine, N-méthyl-2-hydroxyméthyl-pipéridine, 1-(2-hydroxyéthyl)-imidazole, 2-amino-6-méthoxybenzothiazole, 4-aminométhylpyridine, 4-amino-2-méthoxy-pyrimidine, 2-mercaptopyrimidine, 2-mercapto-benzimidazole, 3-amino-1,2,4-triazole, 2-isopropyl-imidazole, 2-éthyl-imidazole, 4-méthyl-imidazole, 2-méthyl-imidazole, 2-éthyl-4-méthyl-imidazole, 2-phényl-imidazole et 4-nitro-imidazole.

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11. Une solution selon les revendications 1-10, dans laquelle la teneur en monomères du groupe D est supérieure à 0 mol% et les monomères sont choisis parmi l'acrylate de 2-hydroxyéthyle, l'acrylate de 2-hydroxypropyle, le méthacrylate de glycidyle, le méthacrylate de 2-hydroxyéthyle, le méthacrylate de 2-hydroxypropyle, l'acide acrylique, l'acide méthacrylique et les produits réactionnels alkoxylés à fonction -OH desdits composés.

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12. L'utilisation de la solution selon les revendications 1-11 dans la production des enduits et des encres d'imprimerie.

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13. L'utilisation selon la revendication 12, en utilisant de 1 à 10 mg de polymère par m² de surface de pigment (BET).

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14. Solides réduits en poudre à incorporer dans des systèmes liquides, enduits du polymère décrit dans les revendications 1-11.

15. Solides selon la revendication 14, dans lesquels la teneur en polymère varie entre 1 et 10 mg par m² de surface de pigment.

16. Dispersions de pigment consistant principalement en un ou plusieurs pigments, un polymère comme décrit dans les revendications 1-11 et de l'eau et/ou un liquide non-aqueux.

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17. Une dispersion de pigment selon la revendication 16, consistant principalement en 10 à 70% en poids de pigment, 1 à 10% en poids dudit polymère et 20 à 89% en poids d'eau et/ou de liquide non-aqueux.